Cyclic Transition States in *cis*- and *trans*-Addition of Chlorine Acetate to Olefinic Substances

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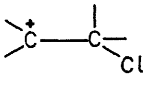
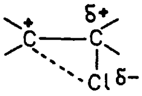
Summary The stereochemical courses of additions of chlorine acetate to some aryl-substituted unsaturated compounds are markedly less stereoselective than the corresponding reactions initiated by electrophilic chlorine.

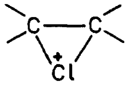
ELECTROPHILIC additions involving simple carbonium ionic, partly bridged, or chloronium intermediates [*e.g.* (I), (II), (III)] in hydroxylic solvents can generally be diverted by added nucleophiles to products involving incorporation of solvent.[1]



(I)



(II)



(III)

Diversions of this kind have been established for addition of Cl_2 in AcOH both to cyclic[2] and to acyclic[3] structures; but it has recently become clear[2,4,5] that a direct addition of Cl_2, in which external nucleophiles do not play a significant role, can also be an important contributor to the reaction path, particularly when the double bond is conjugated with an aryl group.

Proportions of diastereoisomeric acetoxy chlorides formed in addition initiated by chlorine acetate and by molecular chlorine in acetic acid at 25°

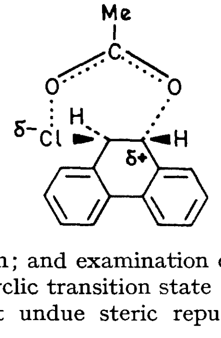
Substrate	Reagent	Added salt	Acetoxy chloride adducts ratio (product of *trans*-addition) : (product of *cis*-addition)
Cyclohexene	ClOAc	—	>100
Acenaphthylene	ClOAc	—	3·0
Acenaphthylene	ClOAc	NaOAc (0·1M)	2·0
Acenaphthylene	Cl_2	—	3·7
Acenaphthylene	Cl_2	NaOAc (0·1M)	7·5
Phenanthrene	ClOAc	—	1·0
Phenanthrene	ClOAc	NaOAc (0·1M)	1·0
Phenanthrene	Cl_2	—	2·2 (ref. 2)
Phenanthrene	Cl_2	NaOAc (0·1M)	4·9 (ref. 2)
Methyl *trans*-cinnamate ..	ClOAc	—	1·6
Methyl *trans*-cinnamate ..	ClOAc	NaOAc (0·1M)	1·7
Methyl *trans*-cinnamate ..	Cl_2	—	5·9 (ref. 3, 5)
Methyl *trans*-cinnamate ..	Cl_2	LiOAc (1·0M)	4·9 (ref. 3, 5)

We have now examined the addition of chlorine acetate[6-8] to some representative olefinic compounds (Table; values for Cl_2 for comparison).

As with Cl_2, addition to cyclohexene is highly stereospecific; addition to the other unsaturated compounds is at best moderately stereoselective, and markedly less so for chlorine acetate than for Cl_2. With phenanthrene and Cl_2, the inclusion of NaOAc in the medium gave some diversion of product towards that of *trans*-addition, as expected if a carbonium ionic intermediate is involved;[2,3] but with chlorine acetate, none of the substrates showed any substantial response to the inclusion of the salt.

All these compounds react with chlorine acetate too rapidly for conventional kinetic measurements. The reaction of ω-nitrostyrene, however, is measurably slow, and a preliminary survey indicates that the kinetic behaviour of this compound is analogous to that observed for aromatic substitution by chlorine acetate in AcOH.[8] The reaction gives two acetoxy chloride adducts, believed to be the diastereoisomeric 1-acetoxy-2-chloro-2-nitro-1-phenylethanes, in the ratio 1·3 : 1, the major component being that which is formed in much greater excess (6·7 : 1) for reaction with Cl_2 in the same solvent.

These results show that the rate of addition of chlorine acetate, like that of Cl_2, responds powerfully to structure, and so the transition states must have much carbonium ionic character. They establish also that the transition states or intermediates leading from chlorine acetate to acetoxy chlorides must be different from those which with Cl_2 lead from the same substrate to the same products in the same solvent. For reactions initiated by chlorine acetate, the failure to alter the product-ratios significantly by addition of NaOAc suggests to us that direct reactions, which can lead to a mixture of *cis*- and *trans*-products both with cyclic and acyclic olefins, play an important part. For addition of chlorine acetate to phenanthrene, four- (as with Cl_2[2,4]) or six-centred transition states could clearly give *cis*-addition; and examination of models suggests that a six-centred cyclic transition state (IV) could give a *trans*-adduct without undue steric repulsions or distortion of



(IV)

valency-angles The importance of the direct reaction may be related to the unexpectedly[8] high reactivity of molecular chlorine acetate in comparison with molecular chlorine and with molecular hypochlorous acid, we hope to delineate this more clearly by detailed kinetic studies, for substitution, both molecular and protonated chlorine acetate were effective reagents [8]

Materials and methods are mainly as described in earlier papers,[2,4,8] products have been identified by ^{1}H n m r spectroscopy No extraneous adducts have been detected, the aromatic systems give also some products of substitution

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[1] *Cf* G Williams, *Trans Faraday Soc* , 1941, **37**, 749

[2] P B D de la Mare, A Singh, E A Johnson, R Koenigsberger, J S Lomas V Sanchez del Olmo, and A M Sexton, *J Chem Soc* (*B*), 1969, 717

[3] M C Cabaleiro and M D Johnson, *J Chem Soc* (*B*), 1967, 565

[4] P B D de la Mare N V Klassen, and R Koenigsberger, *J Chem Soc* , 1961, 5285.

[5] M D Johnson and E N Trachtenberg, *J Chem Soc* (*B*) 1968, 1018

[6] A Schutzenberger, *Compt rend* , 1861, **52**, 135

[7] M Anbar and I Dostrovsky, *J Chem Soc* , 1954, 1094, 1105

[8] P B D de la Mare, I C Hilton, and C A Vernon, *J Chem Soc* , 1960, 4039, P B D de la Mare I C Hilton, and S Varma, *ibid* , p 4044